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(54)发明名称 橡胶聚氨酯复合轮胎的生产方法及装置

(57)摘要

一种涉及橡胶聚氨酯复合轮胎的生产方法及装置。它是将新、旧橡胶轮胎壳表面经处理后，放入模具中加温后抽真空，同时将经加温脱气的液体聚氨酯预混料有脱模剂的真空模腔中，经加压、保压、熟化、降温和脱模即为成品。所用的装置包括：混料注射喷本、注塞、油压机、搅拌泵、电热板、模具和起落架。经本发明以橡胶壳为基，CPU为胎面的聚氨酯或经翻顶、翻新后的复合轮胎，使用寿命相当于橡胶新轮胎的5—10倍。

强，可连续化生产，不但可生产出以橡胶胎壳为基，CPU为胎面的聚氨酯长寿轮胎，同时也可以采用废旧轮胎经处理后，制造出聚氨酯翻新再生长寿轮胎的橡胶聚氨酯复合轮胎的生产方法及装置。

本发明的要点是将新或旧橡胶轮胎壳表面打磨露出带毛刺的新胎面，放入钢模中加热至100～140℃出炉抽真空，将混合好的并经脱气的加热至80～90℃液体聚氨酯原料灌入刷有脱模剂的真空模腔中，待灌满后加压0.1～0.3 MPa，并保压入100～120℃恒温炉经4～6小时熟化后，降温、脱模即为成品。

本发明所使用的聚氨酯原料的选择：

1、聚酯醇（PA）可以是仲羟基线型己二酸乙二醇酯Mn（平均分子量）：500～2000；

2、异氰酸酯可以是4、4二苯基甲烷二异氰酸酯（MDI）。

以上两种原料国内均有生产厂家，年产量几万吨易购买，选用MDI的原因是分子量大、对称性强，产品机械强度好，应注意的是MDI加入量的控制，也就是游离氰酸根—NCO含量的控制，当—NCO增加时，除伸长率降低外，其它性能均有提高，当—NCO含量下降时伸长率增加，其它性能降低较严重，经上百次试验测得最佳—NCO含量为4～6%之间均可采用。

3、扩链剂的选择：热固性灌注聚氨酯（CPU）一般原则如用TDI大都采用胺类扩链剂（MOCA等），当采用MDI时大

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Abstract

This invention is related to a method and apparatus of manufacturing rubber polyurethane composite tyre. The method comprises treating the tread of new or recycled tyre, putting the tyre into a mould, heating and vacuuming the mould, filling the heated and degassed liquid polyurethane into the vacuum mould cavity coated with a releasing agent, applying and holding the pressure, curing, cooling and demoulding. The apparatus includes a mixing injector cylinder, an injecting plug, a hydraulic press, an agitating paddle, an electric heating plate, a mould and an undercarriage. The invention tyre based on rubber carcase and covered by CPU is a composite tyre, its service life is 5-10 times as more as that of new rubber tyre.

Claims

1. A method for manufacturing rubber polyurethane composite tyre comprises putting the recycled tyre having treated tread into a mould, filling polyurethane into the mould, cold curing and demoulding to make the retread tyre, characterized in that the method comprises the following steps: treating the tread of new or recycled tyre into a roughness surface, putting the tyre into the mould, heating the mould to the temperature between 100～140℃ and vacuuming, mixing the liquid polyurethane and filling the degassed and heated to 80～90℃ polyurethane into the vacuum mould cavity coated with a releasing agent, after filling full applying and holding a pressure of 0.1～0.3Mpa, curing 4～6 hours at 100～130℃ in a constant temperature furnace, cooling, demoulding and taking out the retread tyre.

2. The method of claim 1, characterized in that the liquid polyurethane is produced by adding the dried and screened carbon black into the dissolved quantification PA, dewatering the mixture and pouring into a reactor with dissolved MDI, agitating, vacuuming, heating and holding the temperature of 80～85℃ 1.5～2.5 hours to obtain the prepolymer, adding the whole additives into the reactor at vacuum condition, mixing 5-10 minutes and relieving the vacuum.

3. The method of claim 1 or 2, characterized in that the additives in liquid polyurethane contains the following components:

glycol as a chain extender 30～50wt%

trihydroxymethylpropanol or propanetriol as a crosslinker 50～70wt%

the total of the components being 100wt%.

4. An apparatus for manufacturing rubber polyurethane composite tyre comprises a reactor, an injector and a mould, characterized in that a mixing injector cylinder (13) which also acts as a reactor, an agitating paddle (14), a plug (1) which can enter the injector cylinder (13) from upward and inject the polyurethane into the mould (5) with

a hydraulic press (3), a vacuum pump valve (7) and feeding valves (16,18) respectively provided at the upside and downside of the mould (5) being related to the level of 15-45° , a electric heating platen (15) allowing constant temperature control, and a undercarriage (19) for the mould (5).

5. The apparatus of claim 4, characterized in that the polyurethane plug (1) and the injector cylinder (13) assume tight fit.

Description

This invention is related to a method and apparatus of manufacturing rubber polyurethane composite tyre, especially a long working life composite tyre produced by vacuum filling process, which is based on a new or recycled tyre carcase and covered with polyurethane as tread.

Presently, the service life of a new tyre is 0.5-1 year. It is necessary to change the tyre 5-6 times during the period of a vehicle. The billions of old tyres in the world make a great disaster because they have no place to store. Generally the old tyres have a worn tread and a right carcase, the carcase still have a great value in use. Therefore more and more methods and devices for repairing and renewing the tyres have been developed. For example, the Thermal TPU Solvent method, US Patent No.00086942 "The renewing or repairing of tyres of the vehicle (the synthetic thermosol polyurethane)" discovered a method of heating and dissolving the solid thermal polyurethane (TPU) in an organic solvent to obtain a paste, coating the paste to the treated tread, after volatilization forming a polyurethane cover with elasticity. The method has some disadvantages. It uses large quantity of organic solvent to dissolve the solid TPU resulting the environment pollution, especially using a open container to heat and agitate the TPU, and it is dangerous to flame and explode, it is also harmful to the operators. The tyre is obtained from volatilizing solvent. If the thickness of the coating is too large the material will waste a lot, contrarily, if the thickness of the coating is too small it is difficult to reach the physical properties of the tyre. The method synthesizes the liquid TPU with –OH end capping, filling the liquid TPU to form a sheet, cooling to solidify and breaking or extruding to pelletize, drying and dissolving the pellets in a solvent, heating, agitating, dissolving, coating and drying, obtaining the final product. The process is too complex to control and is not safety. The method can be used in thinner coating products because the coating is very thin, the solid content being lower than 30%. Otherwise it is difficult to apply due to the high viscosity. Other methods besides the vacuum coating will bring

in a large number of bubbles to affect the quality. In general, the above method is too complex to control and not safety, resulting from the environment pollution. The coating of the method is uneven in thickness and is poor in quality. The method cannot be applied in large-scale production. The adhesive method, US Patent No.00569192 "The re-synthetic curing plastic rubber for retreading and repairing tyre" (The agglutinant polyurethane synthetic rubber based on polyurethane adhesive), comprises the following steps: treating the surface of the recycled tyre, putting the tyre into a mould, filling the polyurethane into the mould cavity at the room temperature, curing the polyurethane without heating and pressing. The method uses adhesive as tread and increase the cost. It is hard to be accepted by the user and it is hard to meet the need of tyre's inhere properties although the property of the adhesive is good. The cold curing process is no good from the point of view of polyurethane elastomer because the recycled tyre, after treating, contacts the air, especially the humid gas, and adsorbs the hydrone at the tread. Without heating and drying the reaction between water and –NCO group in polyurethane will form CO2 gas. The gas causes to form many micro bubbles sandwiched between the tread and polyurethane. The bubbles separate the tread and polyurethane, just like a buttering layer. Especially, during travelling the bubbles expand due to the friction heat, decreasing the adhesive strength and peeling strength of the interface, even separating the tread from the carcase. It takes long time for the cold curing process. If adding a catalyst in the process for lowering the time, it will cause the side reaction, pooring the properties of the elastomer. Therefore, the US 00569192 method is hard to apply due to the high cost and poor physical properties.

The subject matter of the invention is to provide a method and an apparatus. The process is simple to operate. The product of the process has a great applicability and can be produced continuously. The invention can produce a long working life tyre based on a rubber carcase and CPU tread. The invention can also produce a long working life rubber polyurethane composite tyre from recycled tyre.

The main points of the invention are as follows: treating the tread of new or recycled tyre into a roughness surface, putting the tyre into a mould, heating to 100～140℃ and vacuuming, filling the liquid polyurethane degased and heated to 80～90℃ into the vacuum mould cavity coated with a releasing agent, applying the pressure of 0.1～0.3Mpa after filling full, holding the pressure and curing 4～6 hours at 100～130℃ in a constant temperature furnace, cooling, demoulding and taking out the retread tyre.

The raw material of the polyurethane as follows:

1. Polyester polyol (PA) It may be a linear ethylene glycol adipate with sec-hydroxyl (Mn), the average molecular weight thereof is 1500～2000;

2. Isocyanate It may be a diphenylmethane-4, 4-diisocyanate (MDI).

Both of the above materials are available from inland suppliers. The reasons of selecting MDI are: the molecular of it is great and symmetrical, and the strength of MDI product is good. It should be noted to control the adding amount of the MDI, that is to say controlling the content of the free –NCO. The more of the –NCO content, the higher of the properties of the TPU except the elongation. The less of the –NCO content, the lower of the rest properties but higher of the elongation. After hundreds of test it has been found that the best content of the –NCO is between 4～6%.

3. The chain extender The thermosetting polyurethane (CPU) normally uses TDI with amine chain extender（MOCA）, or uses MDI with alcohol chain extender. A lot of alcohols can be used as the chain extenders in the invention, for example propanediol, ethanediol, dipropylene glycol, diethylene glycol etc. The ethanediol is preferred. During the test the residual deformation of the elastomer with ethanediol as a chain extender is lower, only 3-5%. The residual deformation of normal rubber tyre is 35-40%. In addition the elastomer with ethanediol as a chain extender is less in hysteresis, and lower in temperature rising. The content of the ethanediol is 30～50% based on the total weight of crosslinker and chain extender.

4. The crosslinker The CPU elastomer of the invention uses trihydroxymethyl

propylane or propanetriol with three functional groups etc as the crosslinker. These crosslinkers make the elastomer contain an amount of crosslinking structure. The structure changes some of the physical properties of the elastomer, especially increasing the thermal stability of it. That is very important for the tyre. It is also very important to control the content percent of the crosslinkage. The content of the crosslinking structure can affect the strength, extension at break, modulus, hardness and tearing strength of the elastomer. The content of the crosslinker should be in the range between 50~70% based on the total weight of crosslinker and chain extender. There are two ways to achieve the certain crosslinkage. First is selecting a PA with some side group segmers. Second is using a crosslinker. The invention uses the second method to control the crosslinkage.

The procedure in production:

The dewatered PA →reactor (injector cylinder) →pressing and filling ↘

mould (vacuumized)

The dissolved MDI → prepolymer + additives ↗

The constant temperature furnace:

The temperature of the prepolymer: 75~85℃

The temperature of the mould: 100~140℃

The vacuum: 200~-800 KPa

Formulating of the polyurethane:

PA, Mn 1500~2000 100 parts by weight

MDI, free-NCO content 4~6%

Ethanediol (chain extender) 30~50% (based on the total weight of crosslinker and chain extender)

trihydroxymethyl propylane or propanetriol (crosslinker) 50-70% (based on the total weight of crosslinker and chain extender)

coefficient of diffusion 85~95%

carbodiimide (water-proofing agent) 2～5%

carbon black 2～5%

Physical properties:

tearing strength 200～260Kg/cm^2

breaking elongation 550～600%

residual deformation 3～5%

Shore A hardness 60～70

density 1.28～1.32g/cm^3

abrasion cm3/1.61km 0.03

The invention provides a method for manufacturing polyurethane elastomer from an isocyanate, a polyalcohol and a chain extender. The method can use full prepolymerization process or pseudo prepolymerization process. It requires that the temperature in the reactor should be constant and the agitation should be uniform no matter which process is used. Especially, the agitating must be uniform in short period after adding the chain extender due to the limited time. Otherwise the great difference of physical properties will be appear in the elastomer due to the different hardness in different zone of the elastomer.

PA, as ethylene glycol 1,2-propanediol adipate, is a white or opal solid in ambient temperature. It can be used only in the dissolved and dehydrated state. The MDI is also a white solid. It is added into the reactor after being dosed accurately according to the formulation and dissolved at 40～50℃, and it is agitated in the reactor with vacuuming. The purpose of vacuuming is to prevent air, particularly the humid gas from causing the unsatisfactory side reaction. It takes 2-3 hours to completes the prepolymerization at 75-85℃. In the full prepolymerization the content of free –NCO group must be controlled in the range between 4～6%. In the pseudo prepolymerization the content of free –NCO group must be controlled accurately. After that the additives are sucked from the suction inlet meanwhile maintaining the vacuum. The above formulation without the catalyst or with less catalyst T-12 depends on the operator and production benefit. It may add the catalyst adequately

for easy demoulding without affecting the physical properties of the elastomer.

The keystones for controlling:

1.The volume of the reactant must be lower than 2/3 of the reactor's.

2.The reaction must be carried out in agitating, heating and vacuuming conditions throughout the process.

3.The feeding material must be gauged accurately.

4.Before adding the MDI, the temperature of dissolved and dehydrated PA must be lower than 60℃ because the temperature of the mixture will increase quickly with adding MDI.

5.The viscosity of the prepolymer is related to the water content of PA, the volume of the reactor, the speed of the agitation and the temperature.

The invention combines the mixing step and filling step into a mix-filling step, simplifying the working process. The degased materials fill into the mould in vacuum condition, therefore preventing the humid gas coming into the mould. After filling full the mould a pressure is applied and holded until the curing is completed. The process increases the dense structure of the material, improving the agglutination between the material and the tread, enhancing the mechanical strength and properties of the tread. The invention provides a new method and an apparatus for repairing the recycled tyre. The working life of the repaired tyre is 5-10 times as long as the rubber tyre. The invention increases the benefit of the vehicles, saving the currency for importing the rubber.

The present invention for manufacturing the 825-16 rubber polyurethane composite tyre will be illustrated by reference to the drawing as follow, in which the drawing shows a schematic diagram of the apparatus for producing the rubber polyurethane composite tyre.

The process comprises the following steps: treating the tread of the recycled 825-16 tyre(6) into a roughness new surface, putting the tyre into a sealed mould(5) which is

related to the level 15-45° , heating to 100～140℃ in a furnace, and standing by, adding 500g dried and screened carbon black into 10kg dissolved ethylene glycol 1,2-propanediol adipate(PA), dewatering, pouring the mixture into an injector cylinder(13) which is also as a reactor in which the discharging valve(18) set on the bottom of the cylinder(13) has been closed in advance, pouring 2.9kg dissolved diphenylmethane-4, 4-diisocyanate (MDI) into the cylinder(13), a motor(8) rotating the agitating paddle(14) in the cylinder(13), a vacuum pump vacuuming from the feeding hole(10) located on the cylinder cover(12), (11) being a sight hole, a thermocouple(9) and electric heating platen(15) heating the material to 80～85℃ and holding the temperature 1.5-2.5 hours to obtain a prepolymer, feeding the whole additives (150g ethanediol as a chain extender, 230g propanetriol as a crosslinker, 500g carbodiimide as a water-proofing agent and 10g dibutyltin dilaurate(T-12) as a catalyst) through the feeding hole(10) in a vacuum condition, holding the vacuum at 200-800Kpa, agitating 5-10 minutes, releasing from the vacuum and demounting the cylinder cover(12), adjusting the screw(2) to make the plug(1) located at the upside inlet of the injector cylinder(13), opening the valve(4) on the plug(1) to exhaust and driving the hydraulic press(3), moving the plug(1) to the liquid level of the material, closing the valve(4). The plug (1) made in polyurethane and the mixing cylinder (13) assume tight fit. During the above process the vacuum pump vacuumizes the cavity of the mould(5) through the valve(7) mounted on the upside of the mould, that is to say opening the valve(7) mounted on the upside of the mould and valve(16) mounted on the downside of the mould, connecting the valve(16) and valve(18) with a hose(17), closing the valve(7) to hold the vacuum when beginning the suction, opening the discharge valve(18) mounted on the downside of the cylinder(13), driving the hydraulic press(3) to press and fill the liquid material into the mould cavity slowly, increasing the pressure to 0.1～0.3Mpa with the hydraulic press(3) after filling full, closing the valve(16), lowering down the undercarriage(19), delivering the mould(5) into a furnace, heating and curing 4～6 hours at 100～130℃, taking out the mould, demoulding, checking up and recuring the tyre.